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Overview of This Book

1.1 Why Petrochemical Products Are Important for the Economy

To understand the economic significance of petrochemical products, it is important to first look at some of the history of the petrochemical industry. Aromatics such as benzene, toluene, and the C_8 aromatic isomers have long been of interest to chemists and chemical engineers. In the earliest stages of the chemical industry, these aromatics were recovered by distillation from coal tar, which was a by-product of steel production. In addition to being used as solvents, these basic aromatics could be fairly easily converted into functional derivatives by chlorination, nitration, and similar chemistries, usually in batch operation. Basic intermediates, such as di-chloro benzene isomers, nitro benzene, and chloro-nitro benzene, found their way into agricultural chemicals and pharmaceuticals, among other applications.

In the mid-1800s, styrene (aka styrol) had been found by Erlenmeyer to be capable of producing a dimer, which explained how, when styrene was exposed to air, heat, and sunlight, it would form a hard, rubbery substance. This may have been the first recognition of the potential for aromatics to be useful for polymers. Ethylene followed a similar, but much later pathway with the accidental discovery of polymerization in 1898, followed by industrial polyethylene synthesis in 1933. Ethylene became relatively abundant via steam cracking, and benzene by recovery from naphtha fractions. This led to the use of polyethylene and polystyrene for military purposes during WW II.

Propylene was converted via dimers and trimers into a gasoline component that could be blended with FCC gasoline and naphtha. Cumene, the reaction product of benzene and propylene, was produced in large quantities during WW II as a high-octane component for aviation gasoline, but it was not until near the end of WW II that the Hoch process for oxidation of cumene to phenol and acetone was discovered. Phenol and acetone each have many end uses as solvents or derivatives in pharmaceuticals, agricultural chemicals, and other applications. But more than 65% of the world's phenol is converted into polymers.

After WW II, companies began to focus on ways to sustain economic growth beyond supplying wartime materials, and they focused on emerging consumer goods. With increased automobile production came the need for large amounts of higher octane gasoline. UOP discovered and commercialized catalytic reforming of naphtha to aromatics using a supported platinum catalyst. This process was called Platforming™ and it became a mainstay of refining for its capability to produce significant aromatics along with valuable hydrogen. This development, along with the confluence of polymerization knowledge, and the capacity for production of ethylene and propylene, led to the origins of today's petrochemicals industry. Over the years, polymer chemists have created numerous grades of polyethylene, polypropylene, polystyrene, polycarbonate, and polyethylene terephthalate (PET) for use in the apparel, packaging, automotive, electronics, medical, and numerous other industries. Biodegradable detergents also are derived from hydrocarbon feeds, using benzene and the linear high-molecular weight olefins that are derived from *n*-paraffins. All of these products make use of the abundance of hydrocarbons being produced from crude oil, LPG, and natural gas liquids.

1.1.1 Polyethylene

Today, polyethylene is the most prominent polymer worldwide, with more than 140 million tons per year being produced. It is extremely durable and is used for production of containers, insulators, coatings, pipe, liners, and films. Industries such as packaging, electronics, power transmission, consumer, and household goods produce components or end products made from polyethylene, with significant job creation in finished goods.

1.1.2 Polypropylene

Polypropylene is a thermoplastic polymer with numerous uses, including textiles, packaging, consumer goods, appliances, electrical and manufacturing industries, and automotive and construction industries. More than

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Frank (Xin X.) Zhu, James A. Johnson, David W. Ablin, and Gregory A. Ernst.

90 million tons per year of polypropylene are produced worldwide. The job creation and added value impact is very high in both developed and emerging regions.

1.1.3 Styrene and Polystyrene

Styrene is used in the production of latex, synthetic rubber, and polystyrene resins. Primary categories of styrene are: films, foams, composites, ABS plastic, SAN plastic, SB rubber, and SB latex. It is used in plastic packaging; building insulation; cups and containers; composite products such as tubs, showers, auto body parts, boats, and wind turbines; medical devices; optical fibers; tires; and backing for carpets. Worldwide demand is more than 27 million tons per year.

1.1.4 Polyester

para-Xylene oxidized to terephthalic acid is the primary constituent of polyester fibers, used in fine clothing, carpet staple, and industrial yarn applications such as tire cord. For resin applications such as water or carbonated soft drink bottles, comonomer isophthalic acid, derived from oxidation of *meta*-xylene, is added, in the range of 2–3%. An ethylene derivative, ethylene glycol, is used for cross-linking in the continuous polymerization process. Worldwide PET consumption for fiber, resin, and films is nearly 80 million tons per year.

1.1.5 Polycarbonate and Phenolic Resins

Phenol and acetone are combined to form bisphenol-A, which can then be converted into polycarbonate and epoxide resins. Phenol can also be reacted with formaldehyde to produce phenolic resins, such as bakelite. Polycarbonates are widely used in automotive applications since they are lightweight, durable, and their thermoplastic properties allow them to be easily molded. Worldwide demand for polycarbonate is around 6 million tons per year.

1.1.6 Economic Significance of Polymers

Polymer products permeate nearly every sector of the world's economy. It is very easy to see numerous applications in everyday life throughout the world. Here are a few examples (the list could be much longer):

- Construction
- Furniture
- Transportation
- Clothing
- Sports and leisure
- Food and beverage packaging
- Communications
- Health care
- Electronics

Significant value chains are created that start with the production of aromatics or olefins – the building blocks – in very large production plants located throughout the world. The next step downstream is to convert these petrochemical building blocks into transportable monomers and polymers. For example, *para*-xylene can be converted into purified terephthalic acid (PTA), which can then be transported to facilities where PET fiber or PET resin chips can be produced. The fiber can be shipped to textile mills where it is converted into fabrics, dyed, and then sold to companies that convert it into clothing. The PET resin chips can be shipped to bottle converters, where injection molding is used to make preforms for PET bottles. The preforms can then be blow-molded into bottles that can be used for water, juices, carbonated soft drinks, or other food packaging. Each of these steps requires capital, adds value, and usually takes place on a much smaller scale tonnage-wise than the centralized production of the building blocks.

The move from a large centralized production facility for the building blocks all the way to smaller enterprises that are widely dispersed throughout the world creates significant job opportunities and value added at each step. Many countries that are rich in petroleum resources start by selling crude oil, then build refineries to produce fuels, and then build and operate petrochemical plants that utilize some of the refined hydrocarbons for producing the olefinic and aromatic building blocks. Ultimately, they will create the downstream fabrication industries to gain additional foreign exchange as well as create full employment for the population.

Similarly, countries with large populations that are not rich in petroleum resources, such as China and India, will build significant capacities for refining and petrochemicals based on imported crude oil, and then create the downstream industries that feed the changing consumption patterns of the growing middle class population. There are many factors, which taken together, account for the high importance of petrochemicals to the world's economy. As shown in Figure 1.1, world population continues to grow from just over 7 billion people in 2018 and projected to reach nearly 9 billion people in less than 20 years. Most of this population growth will take place outside OECD countries. World GDP is expected to more than double during this time from $90 trillion to more than $200 trillion. The growth in world GDP will be driven primarily by increases in productivity. This translates to growth in the middle classes of these expanding societies, and more disposable income. The Brookings Institute projects that the world's middle class

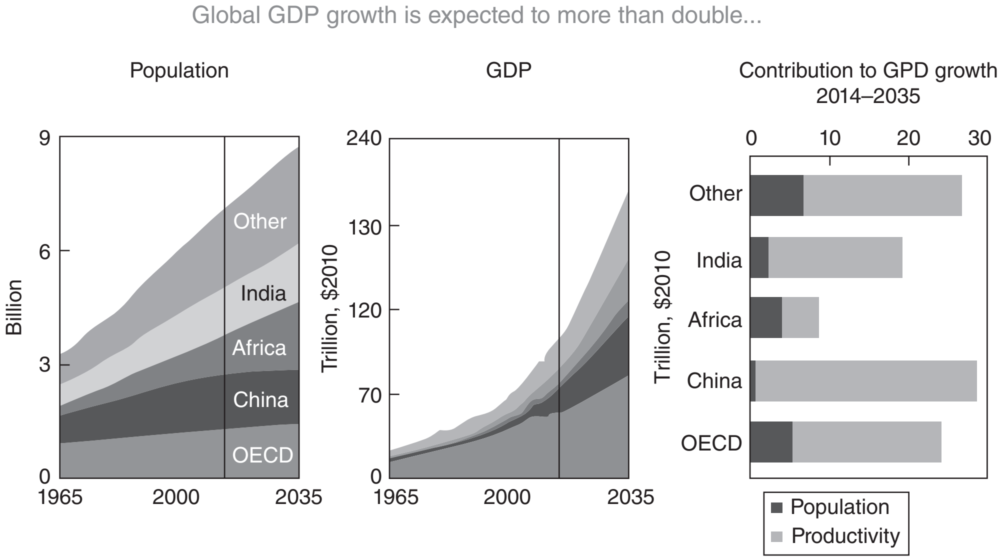

Figure 1.1 World population and GDP growth. *Source:* 2016 Energy Outlook © BP p.l.c 2016.

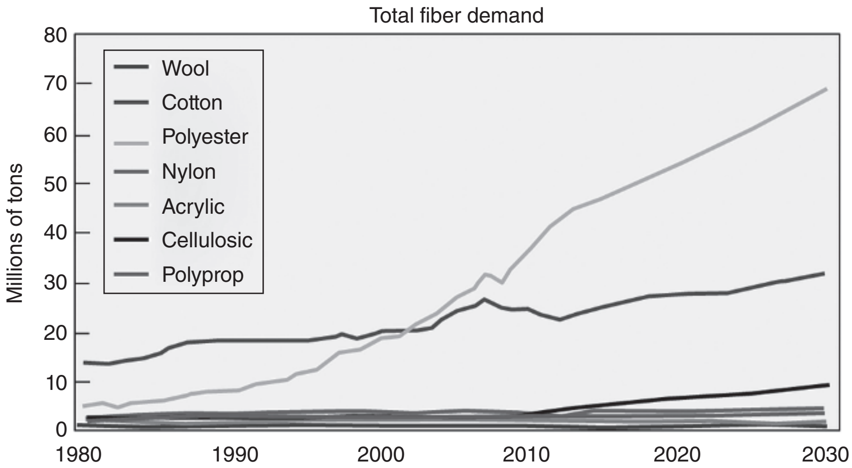

Figure 1.2 Natural and synthetic fiber demand.

will nearly double from 3 billion to more than 5.5 billion people by 2030.

The polyester industries, both fiber and resins, have been the beneficiaries of these changes, and provide a convenient example to illustrate the global economic impact of aromatic petrochemicals. For example, Figure 1.2 shows the world production of various sources of fiber for clothing. Up until about the year 2000, cotton was the dominant fiber, with an annual demand of about 20 million tons. Starting in 2000, the demand for polyester overtook the demand for cotton, and by 2020, is expected to be double that of cotton. Cotton demand has continued to grow at a rate of about 3–4% per year (and is somewhat climate-dependent), whereas polyester fiber demand has grown at 6–7% per year. By 2025, the worldwide demand for polyester fiber will be about 60 million tons per year, whereas the demand for cotton will be only 30 million tons per year. Figure 1.2 also shows the other man-made fibers that compete with cotton.

The per-capita use of man-made vs. natural fibers by region is shown in Figure 1.3. In North America, man-made fiber use was about 22 kg/capita, while China accounted for approximately 13 kg/capita. Polyester accounted for more than 60% of man-made fiber use in North America and nearly 90% of man-made fiber in China.

Nearly 30% of all polyester is converted into resin using solid-state polymerization. Most of this PET resin is used for beverage packaging – that is, bottles for water, carbonated soft drinks, juices, alcoholic beverages, and other food items. These applications, particularly portable water, have enabled significantly greater mobility, where it is possible to travel some distances to work, school, or commerce while still having a clean and reliable supply of water. This

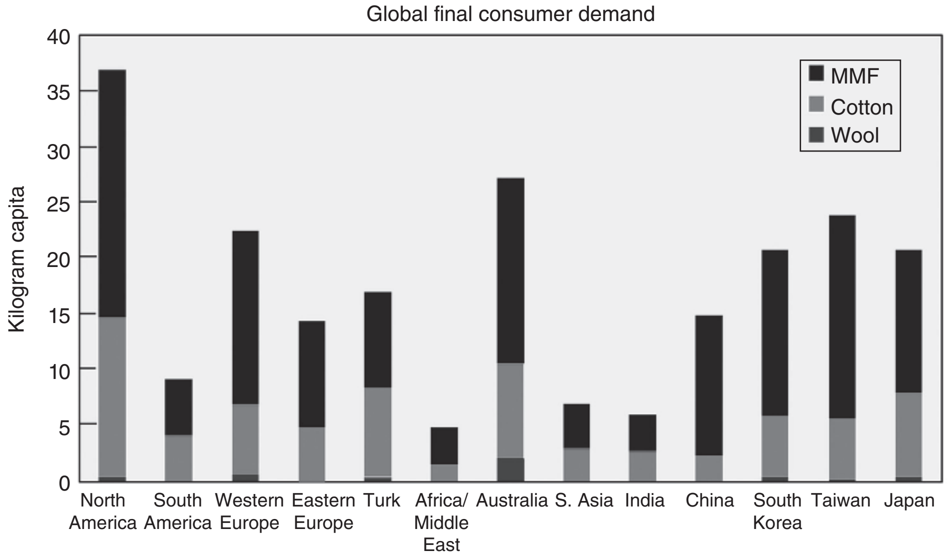

Figure 1.3 Per-capita consumption of fibers by region.

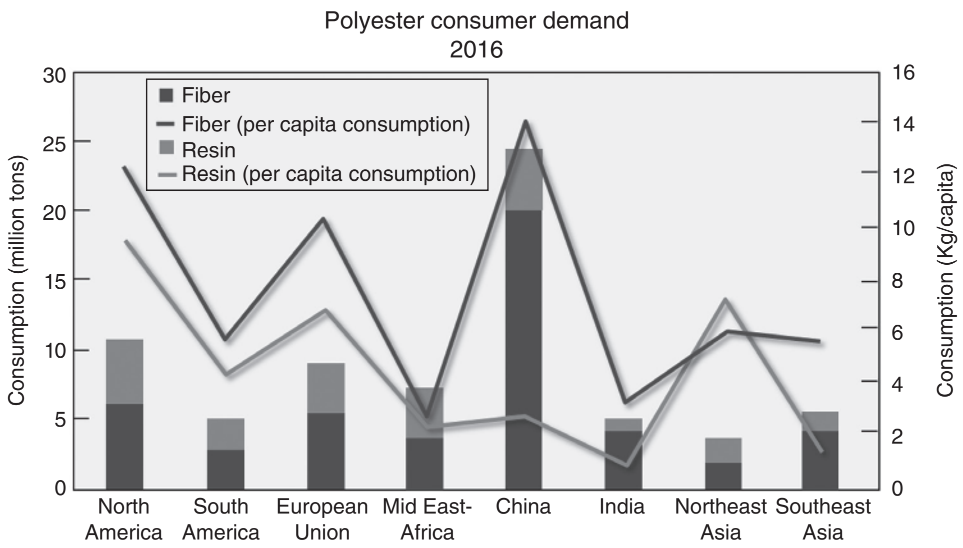

Figure 1.4 PET consumption and per-capita consumption by region.

convenience, in turn, has allowed job growth and expansion of the middle class in many countries. Figure 1.4 provides a breakdown of polyester fiber and resin consumption as well as per-capita usage by region in 2016.

North America, Northeast Asia, and OECD had the highest per-capita usage of resin, in the range of 7–9 kg/capita. China and India, with very large populations had lower per-capita consumption at 1–2 kg/capita, but China's large population still drove the total resin consumption to be very comparable to that of North America at about 5 MM tons. As the middle class grows in China, India, and elsewhere, these per-capita consumption levels are expected to approach those seen in North America, Northeast Asia, and OECD.

Figure 1.4 also shows how important China is to the global consumption of polyester, accounting for nearly 25 million tons in 2016, very close to the combined total of consumption in North America, Northeast Asia, and OECD.

In addition to allowing increased mobility for the population, polyester resin offers significant advantages over glass and aluminum in container weight for beverages and foods. Essentially, the same volume and mechanical strength for retail display purposes can be possible with only a fraction of the container weight compared to glass and aluminum. In addition, distribution and delivery costs from the bottling plants will allow much lower consumption of fuel in delivery vehicles.

Similar detailed examples could be made for styrenics, polycarbonates, urethanes, and polyolefins, all of which have ubiquitous positions in consumer products, transportation, electronics, communications, and construction.

1.1.7 Petrochemicals and Petroleum Utilization

Worldwide, the vast majority of oil production is utilized to produce transportation fuel. Even if gas liquids such as ethane, propane, and butanes are included on a volumetric basis, less than 15% of the world's hydrocarbon resources ended up as petrochemicals in 2016 according to the US Energy Information Agency. During the last 10 or so years, oil prices have been as low as $30/barrel and as high as $100/barrel. Even these higher prices for oil, which translated into costs for naphtha, *para*-xylene (*p*X), and ultimately PET, did not slow down the replacement of natural fiber such as cotton by polyester fiber. Shale oil sources, such as in the United States, can be economically recovered at prices in the $50–60/barrel range and, at this writing, the United States has emerged as a key oil producer at more than 9 MM barrels per day. A large amount of gas liquids, ethane, propane, and butanes are coproduced with shale oil, and have allowed a disconnect to develop between traditional naphtha petrochemical feedstock and these lighter feeds for on-purpose olefin production. As a result, the United States now exports significant amounts of these light hydrocarbons to China, Europe, and other locations, and is able to compete with hydrocarbons produced in the Middle East.

As shown in Figure 1.5, the world consumption of hydrocarbons grew by 36% in the 25 years between 1990 and 2015. Over the next 25 years (2015–2040), world consumption is expected to grow by only about 15%. The highest growth rates are expected in China, India, and the rest of the non-OECD world. Hydrocarbon usage is expected to stay flat or even decline in the United States, OECD, and other highly developed economies. This will be the result of energy efficiency improvements in vehicles, as well as alternatives to internal combustion engines, such as hybrid and electric vehicles (EV's).

Already, many oil refiners in highly developed regions are diverting some of their transportation fuels into petrochemicals, seeking the higher margins that are available from petrochemical intermediates. This is driven by the realization that global demand growth for chemicals will outpace global GDP by 40% over the next several years, as shown in Figure 1.6.

The opportunity to capitalize on the growth rates of petrochemicals is causing those who are investing in new refining capacity to seriously consider adding some processing capability to produce chemicals as well as fuels. While these capabilities add to the capital cost of the project, the high value obtained from the chemical products can significantly improve the net present value and return on investment for a given project. In some cases, such a "pre-investment" may make a great deal of sense.

The prospect of using renewable feed sources has been of interest in transportation fuels, and to some degree in petrochemicals. Renewable fuels such as ethanol, green diesel, or green jet fuel are intended to reduce greenhouse gases, and typically rely on government incentives in order to be economically viable. These can take the form of subsidies, taxes, or renewable fuel credits such as Renewable Identification Numbers (RINs). RINs are a means of accounting for renewable sourced fuels in the US refining industry. Petrochemicals have much lower carbon footprints than fuels, so there have been minimal government incentives to encourage renewable feed sources. There have been a few examples, such as ethylene glycol derived from plant-sourced feeds, but these are largely driven by companies wishing to make a "label claim" that their container incorporates some

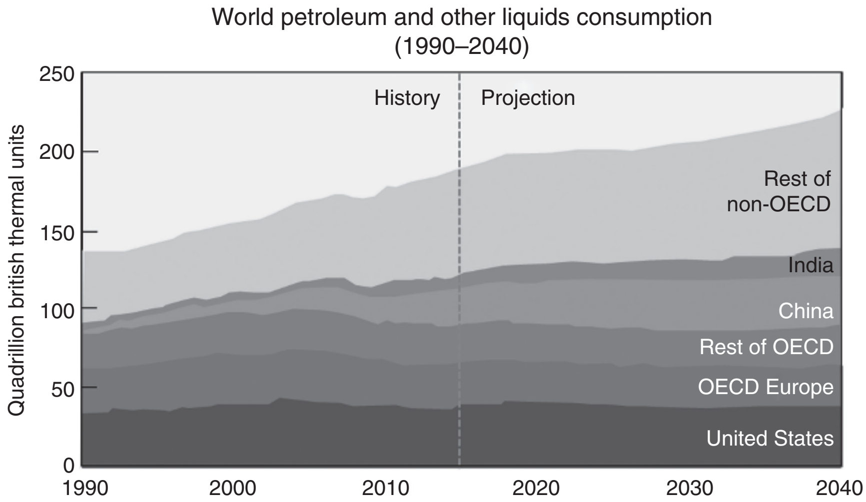

Figure 1.5 World hydrocarbon consumption 1990–2040.

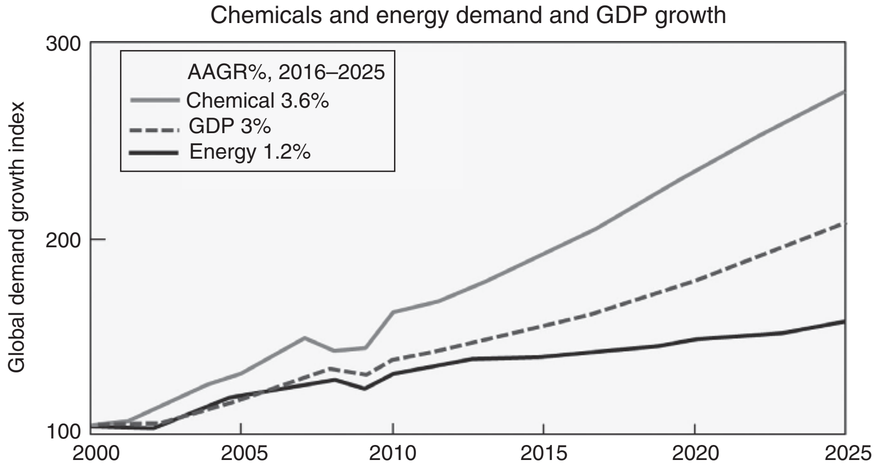

Figure 1.6 Chemicals and energy demand and GDP growth. *Source:* IHS, ExxonMobil 2018 Outlook for Energy, ExxonMobil estimates Birdsall ExMo HP.

renewable-sourced components. The common renewable feed sources, such as plant oils and sugars, are simply too high in price and too uneconomical to convert in high yields. Until there are significant improvements in bioconversion technology and associated polymer performance, hydrocarbon feeds are expected to dominate as sources for petrochemicals.

In summary, the feedstocks for petrochemical products are expected to be abundant, reasonably priced, and will continue to be a small fraction of the total hydrocarbons that are used for transportation fuels. Companies that offer technologies for petrochemical as well as refining will continue to focus on obtaining the highest yields, best use of capital and lowest operating costs for the end products.

1.2 Overall Petrochemical Configurations

In the previous section we concentrated on the economic importance of petrochemicals and how these represent a small fraction of the total amount of hydrocarbons that are processed in industry today. While naphtha fractions from crude oil refining have been dominant, several other sources of feed have gained significance. In order to establish a common frame of reference, Figure 1.7 is a simplified flow diagram that starts with crude oil, and illustrates the link between some common refining products and the associated production of petrochemicals. This also shows how a refiner might find ways to enhance profitability by proceeding along the petrochemical value chain. For example, it may be beneficial to remove benzene from the gasoline pool to be in compliance with environmental regulations. By sending the C_6 stream to an extractive distillation (ED) unit, a high-purity benzene stream can be produced, which could then be combined with propylene produced by the fluid catalytic cracking unit (FCCU) to produce cumene for the petrochemical merchant market. Similarly, from kerosene, the *n*-paraffins could be recovered in high purity and sold into the petrochemicals merchant market to produce biodegradable detergent. The return stream from the *n*-paraffin separation could be sent back into the jet fuel pool.

Some companies focus almost exclusively on petrochemicals from the start and will strive to achieve close integration between refining units and the downstream petrochemical units, as well as between those units that produce olefins and those that produce aromatics. This close integration is shown in Figure 1.8.

Modern steam crackers will be designed with flexibility to use ethane, propane, butanes, and naphtha as feed, with the feed cost and availability as the determining factor. Higher oil prices will favor lighter feeds and vice versa. Pyrolysis gasoline by-product from the steam cracker will have high aromatic content, and can supplement the reformate obtained from the straight-run naphtha for production of the key aromatic products. Although not shown here, the straight-run naphtha can be supplemented with natural gas condensate to further enhance aromatics production. Likewise, a vacuum gas oil (VGO) feedstock hydrocracker can be used to produce supplemental heavy naphtha to further enhance aromatics production. Heavy by-product streams like light cycle oil (LCO) from the FCCU can be converted into additional heavy naphtha or even into a supplemental aromatics stream, depending on the technology.

Production costs of petrochemicals, whether aromatic or olefin, are dominated by feedstock costs. Producers who have integrated refining and petrochemical operations often have the most cost-advantaged positions due to the transfer prices they can set for their key feedstocks. When oil prices are high, producers will place great emphasis on production technologies with the highest yields and lowest utility costs. They will also

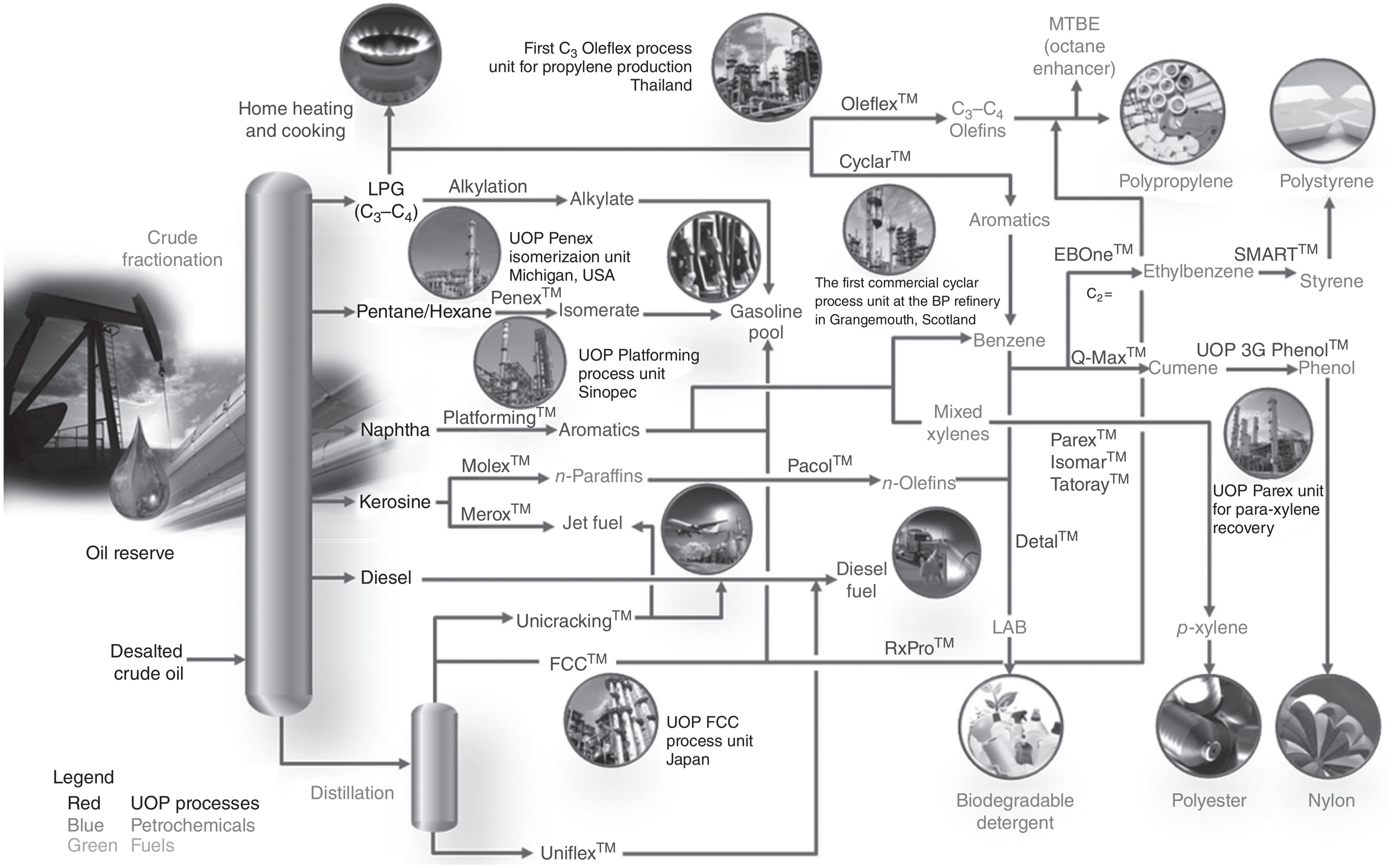

Figure 1.7 Feedstock sources and technologies for petrochemicals and fuels.

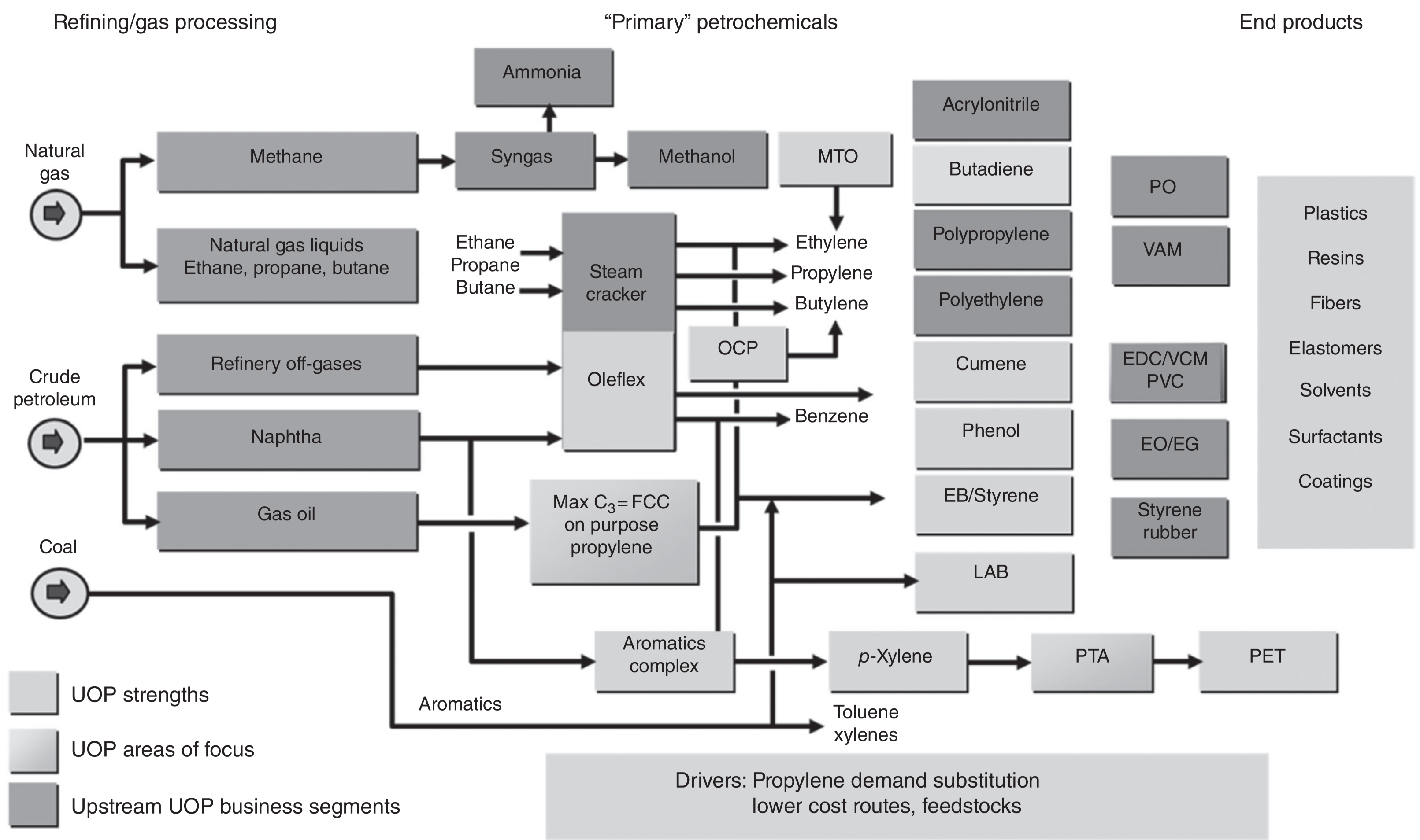

Figure 1.8 Producing petrochemicals from refinery integration.

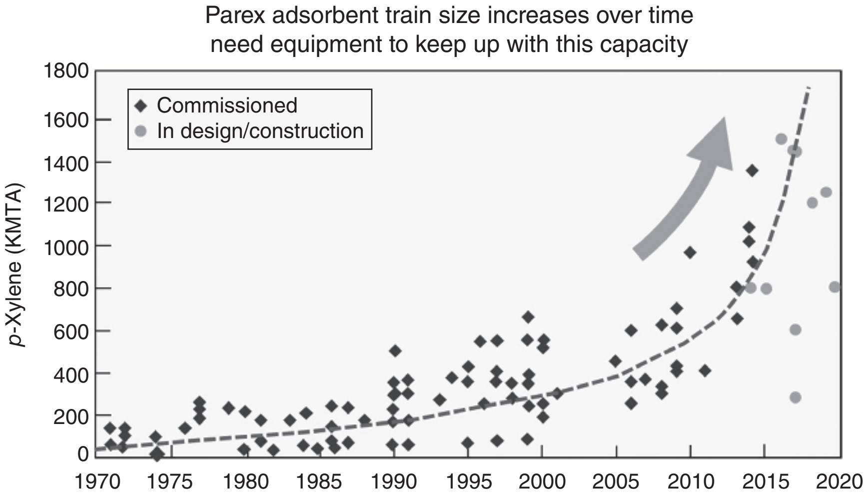

Figure 1.9 Economies of scale in *para*-xylene production.

seek technologies that can economically upgrade low-value by-product streams into petrochemical feeds. Some technologies, such as dehydro-cyclodimerization (DHCD) or toluene methylation (TM) can reduce or eliminate the need for conventional refinery feed streams such as naphtha. Advantageous pricing for LPG or methanol relative to naphtha can make these alternatives very attractive, provided the DHCD or TM technology has good yields. More will be said about this in later chapters of this book.

1.3 Context of Process Designs and Operation for Petrochemical Production

The preceding sections have discussed the macroeconomic drivers behind the rapid growth of the petrochemical industry, its impact in everyday life, some of the basics of how the supply chains of fuels and petrochemicals are linked, as well as the value chains that are created from aromatic petrochemicals. It should be clear that a few molecules – we will call them "monomers" for sake of simplicity – are the backbone of the petrochemical industry. In the next chapters, we will explore in great detail how the quantities and purities of these key monomers are maximized from hydrocarbon streams that contain hundreds of other components. This task of efficiently producing these monomers requires high-performing catalysts and process technologies to transform the hydrocarbon feedstocks into a simpler mixture that can then be efficiently separated into the purified monomers. This is not a trivial task, and companies such as UOP, Axens, ExxonMobil, and BP have spent considerable effort to perfect these technologies over the years. There have been steady advancements in catalysis that have been enabled significant improvements in conversion process technologies. Similarly, advances in separation technologies have enabled greater efficiencies in purification and recovery of these monomers.

On top of these advances in catalysis, separations, and process technologies, the industry has rapidly moved to large-scale "mega-plants" to capture the value in economy of scale, as shown in Figure 1.9. As an example, in 1970, when the UOP Parex™ process was introduced for *p*X, a plant with 100 000 metric tons per year of *p*X capacity was considered to be very large. In 1999, a 400 000 metric ton per year plant was typical. By 2010, the typical *p*X plant size was 1 000 000 metric tons per year. Today, it is not unusual for producers to seek *p*X capacities of 2–2.5 million tons per year for grassroots plants. This evolution toward larger and larger scale plants has driven innovations in equipment such as reactors, adsorption units, fractionators, and other process technologies, complementing the advances in catalysis and separation technologies described earlier.

1.4 Who Is This Book Written For?

This book is intended as a reference on aromatic process technology for students of chemistry and chemical engineering, as well as for industrial business leaders and technologists who are interested in participating in or strengthening their competitive positions in the aromatics industry.